third system, also studied by Wahl and co-workers[22] is the electron self-exchange of ferrocene/ferrocenium and the decamethyl derivative. Both have been studied in dichloromethane. The rate constant at 25 °C and enthalpy of activation are $(4.3 \pm 0.4) \times 10^6$ M^{-1} s^{-1} and 1.7 ± 1.3 kcal/mol for the ferrocene/ferrocenium reaction and $(4.4 \pm 1.0) \times 10^7$ M^{-1} s^{-1} and 2.9 ± 2.0 kcal/mol for the decamethyl derivative. These are much smaller species than the isocyanide complexes, and thus are expected to have larger solvent reorganization barriers.[1] In a recent study by Weaver and co-workers,[3] these reactions and their faster cobalt analogues have been investigated extensively and these authors have argued that solvent dynamics are influencing the rate constants.

Some of the variation in rate constant at each temperature is due to a variation in the total salt concentration. There was no added Bu_4NBF_4 in these experiments thus, the total salt concentration varied along with the Cr(I) complex concentration. When Bu_4NBF_4 was added, the dependence of the rate constant on salt concentration was not large or well-defined, so no attempt was made to adjust the rate constants for this effect. There is a detectable, slight trend toward a lower rate constant with increasing electrolyte concentration. A similar trend is seen with the $Mn(CNR)_6^{+/2+}$ system in chloroform where R is C_6H_{11}.[4] In a system with a neutral and a singly charged complex, $Co(dmg)_3(BF)_2(BF_4)$ (dmg is the doubly deprotonated dimethylglyoxime ligand) and ferrocene in ethylene dichloride,[23] a decrease in k_{12} with added electrolyte is seen and is most pronounced at total electrolyte concentrations below those attainable in the current experiments. This effect has been attributed to ion pairing, with the ion-paired cobalt clathrochleate reacting more slowly then the free cobalt complex.

This work is being extended through study of the $Cr(CNdipp)^{+/2+}$ self-exchange reaction and investigation of complexes of other aryl isocyanides.

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Registry No. $Cr(CNdipp)_6$, 61770-86-3.

Supplementary Material Available: A figure showing the Erying plot (1 page). Ordering information is given on any current masthead page.

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Notes

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164-4630

Pressure and Temperature Effects on the Ruthenocene/Bromoruthenocene Electron Self-Exchange in CD_3CN

Karl Kirchner, Harold W. Dodgen, Scot Wherland,
and John P. Hunt*

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The majority of temperature and pressure studies on electron self-exchange reactions have been carried out on outer-sphere reactions. These experimental and theoretical studies have led to considerable progress in this area. However, little work has been done on inner-sphere electron-transfer processes. The reason for this is the difficulty in finding well-behaved systems in terms of stability, solubility, and suitable time scales for kinetics measurements. Recently, Taube et al.[1] reported on an unusual two-electron, apparently inner-sphere, self-exchange reaction between ruthenocene and various haloruthenocenes in CD_3CN and CD_3NO_2, which is the first known report on this reaction type. Classical inner-sphere reactions involve at least one substitution-labile complex. The activation process involves the expulsion of a ligand during precursor formation, in contrast to an outer-sphere process. In the title reaction both complexes are substitution inert and no initial release of ligand is required. Thus, a quite different behavior is expected. A comparison to the ferrocene–ferrocenium system, for which ΔV^{*} parameters have been obtained recently,[2] may prove to be interesting.

In the present paper we report on kinetics investigations at various temperatures and pressures up to 200 MPa for the ruthenocene–bromoruthenocene electron self-exchange in the solvent CD_3CN.

Experimental Section

Materials. Ruthenocene was obtained from Strem Chemical, Inc., and purified by one vacuum sublimation. $[Ru(cp)_2Br]PF_6$ was prepared as described in the literature.[3] The compound was recrystallized twice from hot acetonitrile/dichloromethane and precipitated with *n*-heptane within a period of 1 h. All solvents used for the purification of $Ru(cp)_2Br^+$ were purchased from J. T. Baker Chemicals and purified by literature methods.[4] The deuterated acetonitrile (99.7% D) was purchased from MSD Isotopes and was used as obtained. Solutions were prepared within a dry-argon-atmosphere glovebox.

^1H NMR Experiments. The temperature-dependence data were recorded by the use of a Nicolet NT200WB instrument. The acquisition parameters were a 4.5-μs pulse with a 500-ms postacquisition delay, a 2000-Hz sweep width, an 8K block size, and 256 pulses. The high-pressure measurements were performed by using a Bruker WH-90 spectrometer. For the variable-pressure experiments, a nonspinning sample tube, similar to one described in the literature,[5] was used. It consisted of a 3.5-cm section taken from the bottom of a 5-mm NMR tube and extended with ca. 3 cm of heat-shrinkable Teflon tubing to transmit pressure. This was plugged with a tapered glass rod. A total of 200 scans (1.5-μs pulse, 4-s repetition rate, 4K data points, 1000-Hz sweep width) were used. The digitized data from both spectrometers were transferred to a personal computer based on an 8286 processor running Quick Basic and treated by a complete line-shape analysis to obtain the second-order electron self-exchange rate constants. The theoretical spectra were calculated by using a modified Bloch's equation for two exchanging sites.[6] The nonlinear least-squares program adjusted the pseudo-first-order electron jump rate constant to minimize reduced χ^2. With this procedure it was possible to determine the rate constant within ±5%. NMR line widths and chemical shifts, relative to tetramethylsilane, for the pure compounds were measured at various temperatures and pressures. Both the temperature and the pressure dependence of their shifts and widths were negligible over the range studied. Mixtures of the two complexes were stable for several days.

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Table I. Enthalpies and Entropies of Activation and 1 atm of Pressure Rate Constants[a]

anion	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/(mol deg)	$10^{-3}k_0$, $M^{-1}\,s^{-1}$
PF_6^- [b]	8.0 ± 0.3	−16.3 ± 0.8	1.6
ClO_4^- [c]	8.5 ± 0.2	−14.9 ± 0.3	1.7
BF_4^- [d]	8.4 ± 0.2	−15.2 ± 0.2	1.7

[a] Six points in the temperature range 20–70 °C; k_0 is for 20 °C. [b] $[Ru(cp)_2]$ = 16.7 mM; $[Ru(cp)_2Br]PF_6$ = 19.1 mM. [c] $[Ru(cp)_2]$ = 7.6 mM; $[Ru(cp)_2Br]ClO_4$ = 7.2 mM. [d] $[Ru(cp)_2]$ = 10.2 mM; $[Ru(cp)_2Br]BF_4$ = 9.3 mM.

Table II. Volume of Activation and 1 atm of Pressure Rate Constants

T, °C	no. of points[a]	$\Delta V^\ddagger$, cm^3/mol	$10^{-3}k_0$, $M^{-1}\,s^{-1}$
33.5[b]	10	−2.9 ± 0.1	3.1
41.7[c]	8	−2.7 ± 0.4	5.2
41.9[b]	9	−2.9 ± 0.1	4.6
43.7[d]	9	−3.1 ± 0.2	5.0
54.7[d]	11	−3.3 ± 0.2	9.0

[a] Pressures in the range 0.1–200 MPa. [b] $[Ru(cp)_2]$ = 8.9 mM; $[Ru(cp)_2Br]PF_6$ = 8.4 mM. [c] $[Ru(cp)_2]$ = 8.6 mM; $[Ru(cp)_2Br]PF_6$ = 10.3 mM. [d] $[Ru(cp)_2]$ = 12.5 mM; $[Ru(cp)_2Br]PF_6$ = 8.8 mM.

The temperature-dependence data were fit to the Eyring equation. The errors were calculated from the standard deviation in k, the second-order rate constant. The volume of activation, $\Delta V^\ddagger = -RT(\partial \ln k/\partial P)_T$, was found by plotting ln k vs pressure (0–200 MPa). For all pressure-dependent data a simple linear fitting procedure could be used. The errors were derived from the scatter about the fit lines.

Results and Discussion

The results of the temperature and pressure dependences are summarized in Tables I and II. Activation enthalpies and entropies are similar to those obtained by Taube et al.,[1] 9.3 ± 1.1 kcal/mol and −12 ± 4 cal/(mol deg), by using CD_3NO_2 as the solvent and PF_6^- as the counterion. There is essentially no dependence on the counter ion, as might be expected in acetonitrile in which little ion pairing is expected. The volume of activation is -3.0 ± 0.2 $cm^3\,mol^{-1}$, independent of temperature in the range 34–55 °C.

The factors that control the volume of activation for an outer-sphere electron-transfer reaction involving a neutral reactant arise primarily from solvation contributions.[7,8] These can be considered within a Marcus theory formalism or more simply by a consideration of just the electrostriction of the solvent. An inner-sphere reaction should include the same solvation terms, but also requires consideration of any coordinated solvent that is displaced and the particular structure of the inner-sphere transition state. Since the system studied here does not involve coordinated solvent displacement and is of the simplest 0/+ charge type, it can be compared with the ferrocene–ferrocenium system with the added consideration for the inner-sphere transition-state structure. Our studies of that system to date suggest $\Delta V^\ddagger$ values of −5 to −8 $cm^3\,mol^{-1}$.[2] Only positive values can be predicted from simple solvent electrostriction arguments. A somewhat more negative value is predicted by the Marcus theory formalism, by using estimates of some of the solvent parameters. The similarity of the two measured values is probably fortuitous, but may indicate that reactant juxtaposition and charge type control $\Delta V^\ddagger$. The ruthenium reaction is about 3 orders of magnitude slower, primarily because of a much greater enthalpy of activation. Also, it involves ring reorientation and the bridge bond formation. The iron case involves an especially rapid reaction, and it has been suggested[9] that the transition state involves a stacked ring geometry.

The ruthenocene–haloruthenocene system is particularly interesting because it involves multiple electron and halogen transfer and it is amenable to study. We are pursuing further studies on it and the decamethyl derivative. Solvent and halogen variation may prove especially interesting since bromoruthenocene is soluble and stable only in solvents of moderate dielectric constant and high acceptor ability. This indicates a significant influence of the bromine atom on the solvation, and this atom must be desolvated for electron-transfer bridge formation. Studies of ion pairing through the use of high anion concentrations or lower dielectric solvents will establish whether this class of reactions behaves as do outer-sphere processes.

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Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas 76129

Reactions of an Azidoborane with Phosphines: Synthesis of (Borylimino)phosphoranes

Bei-Li Li, Purnendu Mukherjee, and Robert H. Neilson*

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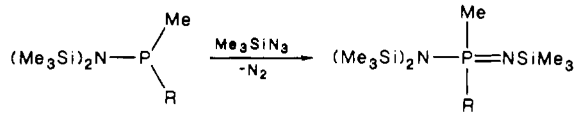
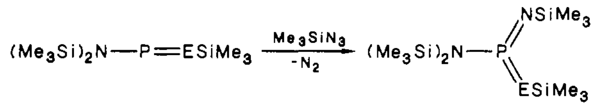
The oxidation of organophosphines with covalent azides, the well-known Staudinger reaction,[1,2] is a very useful method for preparing the pentavalent iminophosphorane derivatives ($R_3P{=}NR$). The high thermal stability and ready availability of silyl azides[3] makes this method particularly useful for the synthesis of *N*-silylphosphoranimines such as those derived from either the (silylamino)phosphines (eq 1)[4] or the two-coordinate methylene-[5] and iminophosphines[6] (eq 2).



$$(Me_3Si)_2N{-}P(Me)(R) \xrightarrow[-N_2]{Me_3SiN_3} (Me_3Si)_2N{-}P(Me)(R){=}NSiMe_3 \quad (1)$$

R = Me, Ph



$$(Me_3Si)_2N{-}P{=}ESiMe_3 \xrightarrow[-N_2]{Me_3SiN_3} (Me_3Si)_2N{-}P({=}NSiMe_3)({=}ESiMe_3) \quad (2)$$

E = CH, N

Much of our recent work has involved the preparative chemistry of new Si–N–P,[7] Si–N–B,[8,9] and B–N–P[10] compounds as possible

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